Supporting Information

2: Compound 10 (0.5g, 1.3 mmoles) was dissolved in anhydrous, degassed, CH_2Cl_2 (0.005 M). The catalysts $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (0.06 g, 0.07 mmoles) was added under an Ar atmosphere and the reaction was heated to 40 °C for 12 h. The reaction was cooled to room temperature and quenched by addition of ethyl vinyl ether. The crude oil was purified by column chromatography (SiO_2: ethyl acetate) to yield **2** as a colorless oil (0.23 g, 50% yield). Characterization for this compound has been reported previously (see ref 10a).

5: A solution of ethylene glycol (152.1 ml, 2.73 moles), 5-bromo-1-pentene (50 g, 0.335 moles) and H_2O containing NaOH (53.2 g, 1.36 moles, in 53 ml H_2O) was heated at 80 °C for 12 hours. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO_2: hexanes/ethyl acetate 4:1) to yield the monoalkylated product as a colorless oil (33.6 g, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.79 (m, center, 1H), 5.03-4.92 (broad m, 2H), 3.75 (t, J = 4.7 Hz, 2H), 3.56 (t, J = 4.8 Hz, 2H), 3.51 (t, J = 6.6 Hz, 2H), 2.12-2.19 (multiplet, 2H), 1.72 (quintet, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.15, 114.78, 71.81, 70.63, 61.84, 30.28, 28.78. HRMS-EI (m/z): [M + e] calcd for $C_7H_{14}O_2$, 130.0994; found, 130.0996.

The monoalkylated product (18 g, 138.5 mmoles) and triethylamine (28.9 ml, 207.7 mmoles) were dissolved in CH_2Cl_2 (500 ml, 0.25 M) and cooled to 0 °C. A solution of mesyl chloride (16.1 ml, 207.68 mmoles) in CH_2Cl_2 (50 ml) was added slowly. The reaction was gradually warmed to room temperature and stirred overnight. The reaction mixture was diluted with water and washed with methylene chloride three times, to give a crude product, which was purified by column chromatography (SiO_2: hexanes/ethyl acetate 3:1) to yield **5** as a colorless oil (23.2 g, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.81 (m, center, 1H), 5.06-4.97 (broad m, 2H), 4.37 (t, J = 4.7 Hz, 2H), 3.70 (t, J = 4.7 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H), 3.06 (s, 3H), 2.13 (q, J = 7.1 Hz, 2H), 1.69 (quintet, J = 7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.97, 115.01, 70.81, 69.25, 68.50, 37.69, 30.14, 28.72. HRMS-FAB (m/z): [M + H] calcd for $C_8H_{17}O_4S$, 209.0848; found, 209.0848.

6: Compound **5** (12 g, 57.7 mmoles), 4-cyanophenol (7.56 g, 63.5 mmoles), and potassium carbonate (11.9 g, 86.5 mmoles) were suspended in anhydrous DMF (575 ml, 0.1 M). The reaction mixture was heated to 80 °C and stirred for 3 days. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO_2: hexanes/ethyl acetate 9:1) to yield the alkylated product as an orange oil (13.4 g, 88% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (d, J = 9.0 Hz, 2H), 6.98 (d, J = 9.0 Hz, 2H), 5.82 (m, center, 1H), 5.06-4.95 (m, broad, 2H), 4.17 (t, J = 4.8 Hz, 2H), 3.80 (t, J = 5.1 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H), 2.13 (q, J = 7.2 Hz, 2H), 1.71 (quintet, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.36, 138.27, 134.13, 119.40, 115.54, 115.08, 104.28, 71.12, 69.05, 67.80, 30.34, 28.90. HRMS-EI (m/z): [M + e] calcd for $C_{14}H_{17}NO_4$, 231.1259; found, 231.1248.

The alkylated product (11.3 g, 48.7 mmoles) was dissolved in anhydrous THF (490 ml, 0.1 M) and cooled to 0 °C. Lithium aluminum hydride (5.5 g, 146.0 mmoles) was added slowly, piecewise, to the reaction mixture. The reaction was warmed to 76 °C and refluxed under an argon atmosphere for 12 hours. The reaction was quenched by addition of 5.5 ml of H_2O, followed by addition of 5.5 ml of NaOH(aq) (15 %) followed by addition of 11 ml of H_2O. The reaction mixture was diluted with ethyl ether and washed with water three times to yield compound **6** as a yellow oil (10.9 g, 94% yield). No further purification was necessary. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 5.86 (m, center, 1H), 5.09-4.98 (m, broad, 2H), 4.15 (t, J = 5.1 Hz, 2H), 3.84 (s, 2H), 3.81 (t, J = 4.8 Hz, 2H), 3.58 (t, J = 6.9 Hz, 2H), 2.17 (q, J = 7.8 Hz, 2H), 1.79-1.70 (m, broad, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.92, 138.38, 135.92, 128.35,114.93, 114.86, 70.99, 69.39, 67.65, 30.35, 28.94. HRMS-EI (m/z): [M + e] calcd for $C_{14}H_{21}NO_2$, 235.1572; found, 235.1569.

7: Compound **2** (12 g, 57.7 mmoles), 4-hydroxybenzaldehyde (7.7 g, 63.5 mmoles), and potassium carbonate (12.9 g, 86.5 mmoles) were suspended in anhydrous DMF (575 ml, 0.1 M). The reaction mixture was heated to 80 °C and stirred for 3 days. The reaction mixture was diluted with water and washed with ethyl acetate three times to give a crude product, which was purified by column chromatography (SiO_2: hexanes/ethyl acetate 9:1) to yield **7** as an orange oil (12.4 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.88 (s, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), 5.81 (m, center, 1H), 5.05-4.93 (m, broad, 2H), 4.20 (t, J = 4.8 Hz, 2H), 3.80 (t, J = 4.8 Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 2.13 (q, J = 6.6 Hz, 2H), 1.70 (quintet, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.95, 164.07, 138.27, 132.09, 130.20, 115.06, 115.03, 71.07, 69.07, 67.94, 30.32, 28.89. HRMS-EI (m/z): [M + e] calcd for $C_{14}H_{18}O_3$, 234.1256; found, 234.1258.

8: A mixture of compound **6** (10.7 g, 45.3 mmoles) and compound **7** (10.7 g, 45.3 mmoles) in toluene (450 ml, 0.1 M) was heated under reflux for 12 hours using a Dean-Stark apparatus. The solvent was evaporated under reduced pressure to give the immine as a yellow oil (20.5 g). This product was immediately used in the next step without purification.

The imine (20.5 g, 45.3 mmoles) was dissolved in MeOH (450 ml, 0.1 M). After portion-wise addition of sodium borohydride (5.2 g, 135.8 mmoles), the reaction mixture was stirred for 4 hours. The solvent was evaporated under reduced pressure and the crude residue was partitioned between CH_2Cl_2 (400 ml) and 2M NaOH solution (400 ml). The aqueous layer was further washed with CH_2Cl_2 (400 ml). The organic phases were combined and washed with NaCl (sat.) and dried over $MgSO_4$. Filtration, followed by evaporation gave the crude product, which was purified by column chromatography (SiO_2: hexanes/ethyl acetate + 10% Et_3N 4:1) to yield the amine as a yellow oil (14.8 g, 72% yield over two steps). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, J = 8.7 Hz, 4H), 6.89 (d, J = 8.7 Hz, 4H), 5.83 (m, center, 2H), 5.07-4.95 (m, broad, 4H), 4.12 (t, J = 4.8 Hz, 4H), 3.79 (t, J = 5.1 Hz, 4H), 3.73 (s, 4H), 3.55 (t, J = 6.6 Hz, 4H), 2.15 (q, J = 6.9 Hz, 4H), 1.72 (quintet, J = 7.2, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.06, 138.42, 132.83, 129.47, 114.97, 114.75, 71.03, 69.42, 67.65, 52.64, 30.39, 28.98. HRMS-FAB (m/z): [M + H] calcd for $C_{28}H_{40}NO_4$, 454.2957; found, 454.2980.

The amine (14.8 g, 32.7 mmoles), di-tert-butyl dicarbonate (15.0 ml, 65.4 mmoles) and 4-dimethylaminopyridine (cat.) were dissolved in CH_2Cl_2 (350 ml, 0.1 M) and allowed to stir at room temperature overnight. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (SiO_2: hexanes/ethyl acetate 9:1) to yield **8** as a pale yellow oil (15.0 g, 73 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.118 (app. s, broad, 4H), 6.88 (d, J = 8.7 Hz, 4H), 5.83 (m, center, 2H), 5.08-4.95 (m, broad, 4H), 4.28 (m, broad, center, 4H), 4.12 (t, J = 5.1 Hz, 4H), 3.79 (t, J = 5.4 Hz, 4H), 3.56 (t, J = 6.6 Hz, 4H), 2.15 (q, J = 8.1 Hz, 4H), 1.72 (quintet, J = 6.9 Hz, 4H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.30, 156.15, 138.42, 130.49, 129.46, 128.93, 114.99, 114.85, 80.08, 71.60, 69.43, 67.68, 48.35, 30.41, 29.00, 28.69. HRMS-FAB (m/z): [M + e] calcd for $C_{33}H_{47}NO_6$, 553.3403; found, 553.3394.

9: Compound **8** (3 g, 5.4 mmoles) was dissolved in anhydrous, degassed CH_2Cl_2 (0.005M). The catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru{=}CHPh$ (0.2 g, 0.3 mmoles) was added under a dry Ar atmosphere and the reaction was heated to 40 °C for 12 h. The reaction was allowed to cool to room temperature and quenched by addition of ethyl vinyl ether. The reaction was stirred for an additional 30 min. Solvent was removed under reduced pressure and the crude oil was purified by column chromatography (SiO_2: hexanes/ethyl acetate 9:1) to yield the protected macrocycle as a colorless oil (3g, 52 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.96 (m, broad, 4H), 6.70 (m, broad, 4H), 5.42 (m, broad, 2H), 4.34-4.46 (m, broad, 4H), 4.02-4.11 (m, broad, 4H), 3.73 (t, J = 4.5 Hz, 4H), 3.52 (t, J = 6.3 Hz, 4H), 2.05-2.19 (m, broad, 4H), 1.64 (quintet, J = 6.6 Hz, 4H), 1.49 (s, 9H), 1.50 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.18, 130.41, 130.18, 129.22, 114.90, 80.06, 70.81, 69.48, 68.03, 51.46, 29.59, 29.28, 28.68. HRMS-FAB (m/z): [M + e] calcd for $C_{31}H_{43}NO_6$, 525.3090; found, 525.3085.

The protected macrocycle (3g, 5.7 mmoles) was added to a suspension of Pd/C (cat.) in EtOAc (0.05M). The reaction was stirred under an atmosphere of hydrogen for 6 h. The reaction mixture was filtered through celite to remove Pd/C and evaporated under reduced pressure. The product required no further purification. The hydrogenated macrocycle was obtained as a colorless oil (2.9 g, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (m, broad, 4H), 6.75 (m, broad, 4H), 4.43 (s, broad, 2H), 4.34 (s, broad, 2H), 4.09 (t, J = 4.5 Hz, 4H), 3.74 (t, J = 3.9 Hz, 4H), 3.52 (t, J = 6.3 Hz, 4H), 1.56 (quintet, J = 6.9 Hz, 4H), 1.44-1.32 (m, broad, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.19, 130.11, 129.17, 114.72, 80.06, 71.56, 69.45, 68.08, 51.50, 29.80, 29.30, 28.67, 26.12. HRMS-FAB (m/z): [M + H] calcd for $C_{31}H_{46}NO_6$, 528.3325; found, 528.3308.

The hydrogenated macrocycle (2.9 g, 5.5 mmoles) and trifluoroacetic acid (6.3 g, 55.0 mmoles) were dissolved in MeOH (0.05M). The reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated to dryness under reduced pressure. The crude residue was dissolved in CH_2Cl_2 and ammonium hexafluorophosphate (9.0 g, 549 mmoles) was added. The mixture was stirred at room temperature for 3 h. to complete the ion exchange. The reaction mixture was washed with H_2O (2 x 100 ml), and the organic phase was dried over magnesium sulfate, filtered and the solvent was evaporated to dryness under reduced pressure. No further purification was necessary. The dibenzylammonium macrocycle **9** was obtained as an off-white sticky solid (2.9 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10 (d, J = 8.7 Hz, 4H), 6.94 (d, J = 8.7 Hz, 4H), 4.18 (t, J = 4.5 Hz, 4H),

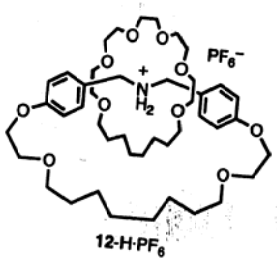
4.16 (t, J = 4.5 Hz, 4H), 3.72 (t, J = 4.5 Hz, 4H), 3.46 (t, J = 6.0 Hz, 4H), 1.90 (s, broad, 2H), 1.47 (q, J = 6.75 Hz, 4H), 1.28 (m, broad, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.37, 130.50, 126.80, 116.51, 71.51, 69.86, 68.30, 50.96, 29.90, 29.62, 26.30. HRMS-FAB (m/z): [M + H] calc'd for $C_{26}H_{38}NO_4$, 428.2801; found, 428.2789.

10: Sodium hydride (60% in mineral oil, 7 g, 182.6 mmoles) was suspended in anhydrous THF (183 ml, 0.1 M). 4-pentene-1-ol (4.15 ml, 40.3 mmoles) was added slowly as a solution in THF (20 ml). The mixture was refluxed under a dry Ar atmosphere for 1 h. The reaction was cooled to 0 °C and pentaethylene glycol ditosylate (10 g, 18.3 mmoles) was added slowly as a solution in THF (20 ml). The reaction was warmed to room temperature and stirred under an Ar atmosphere for 5 days. The reaction mixture was quenched by addition of MeOH. The solvent was evaporated under reduced pressure and partitioned between CH_2Cl_2 (200 ml) and brine (200 ml). The aqueous phase was extracted one additional time with CH_2Cl_2 (200 ml). The organic phases were combined, dried over magnesium sulfate, filtered and the solvent was evaporated under reduced pressure. The crude oil was purified by column chromatography (SiO_2: ethyl acetate) to yield **10** as a colorless oil (3.42 g, 50% yield). Characterization for this compound has been reported previously (see ref 10a).

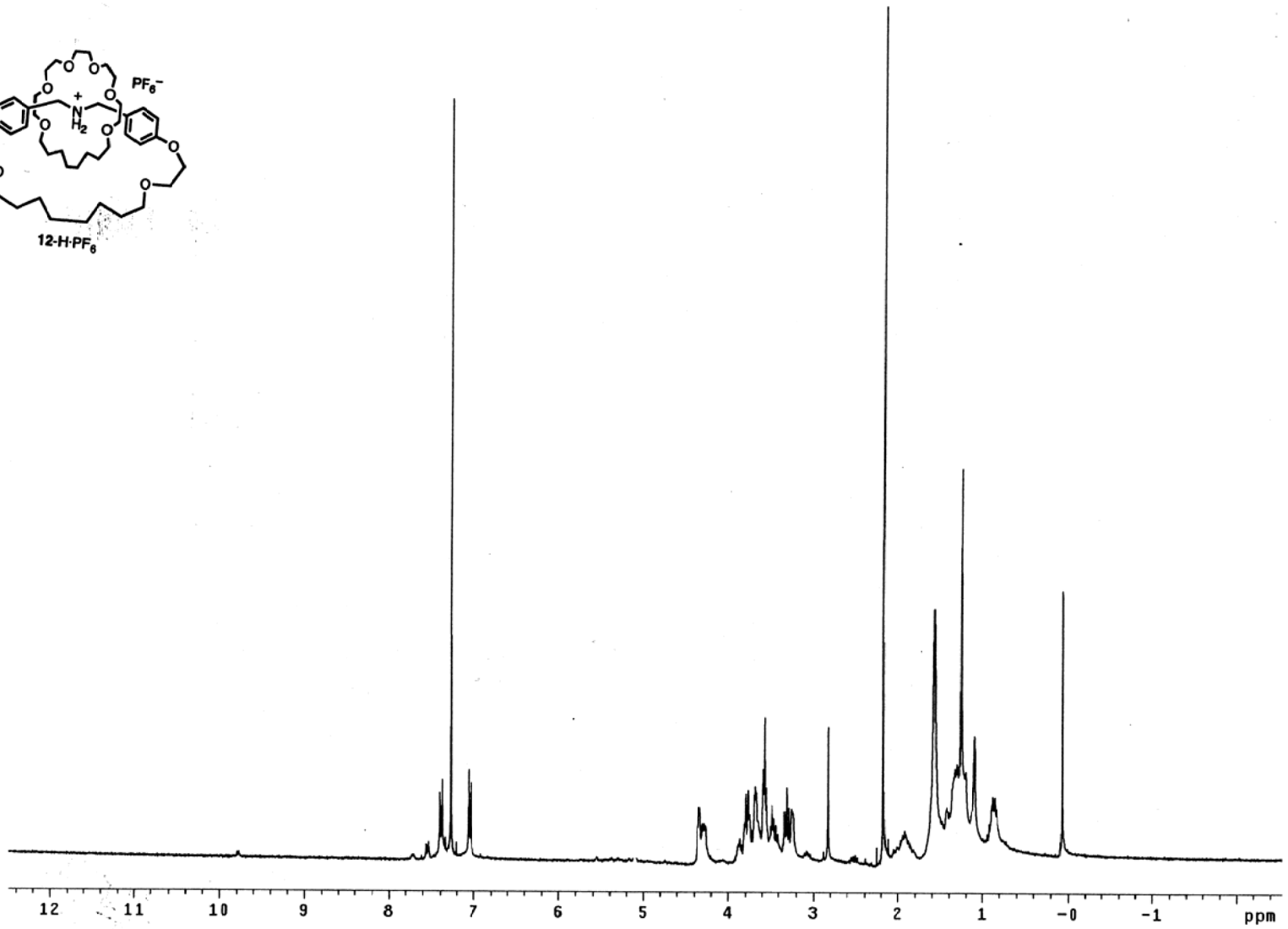
11-H·PF_6: Compound **9** (1.5g, 2.6 mmoles) and compound **10** (0.98g, 2.6 mmoles) were dissolved in anhydrous, degassed, CH_2Cl_2 (0.005M). The catalyst $(H_2IMes)(PCy_3)(Cl)_2Ru$ =CHPh (0.11g, 0.13 mmoles) was added under an Ar atmosphere and the reaction was heated to 40°C for 12 h. The reaction was cooled to room temperature and quenched by addition of ethyl vinyl ether. The reaction was stirred for an additional 30 min. Solvent was removed under reduced pressure and the crude oil was purified by tritration with ethyl ether (2 x 10 ml), followed by column chromatography (SiO_2: CH_2Cl_2/MeOH 99:1) to yield **11**-H·PF_6 as a light brown sticky solid (1.3g, 52-75% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 (d, J = 8.4 Hz, 4H), 7.04 (d, J = 8.4 Hz, 4H), 5.38 (m, 2H), 4.34 (m, 4H), 4.23 (m, 4H), 3.76 (s, 8H), 3.67 (t, J = 3.9 Hz, 4H), 3.62 (t, J = 6.9 Hz, 4H), 3.52 (m, 4H), 3.30 (t, J = 7.2 Hz, 4H), 3.23 (m, 4H), 2.91 (s, 4H), 2.11 (m, 4H), 1.73 (quintet, J = 6 Hz, 4H), 1.32 (m, 4H), 1.26 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.18, 132.21, 131.07, 123.43, 115.85, 71.90, 71.57, 70.77, 70.47, 69.93, 69.61, 69.32, 67.82, 51.49, 30.43, 30.04, 29.80, 28.60, 28.37, 25.92. HRMS-FAB (m/z): [M +] calcd for $C_{44}H_{72}NO_{10}$, 774.5168; found, 774.5156.

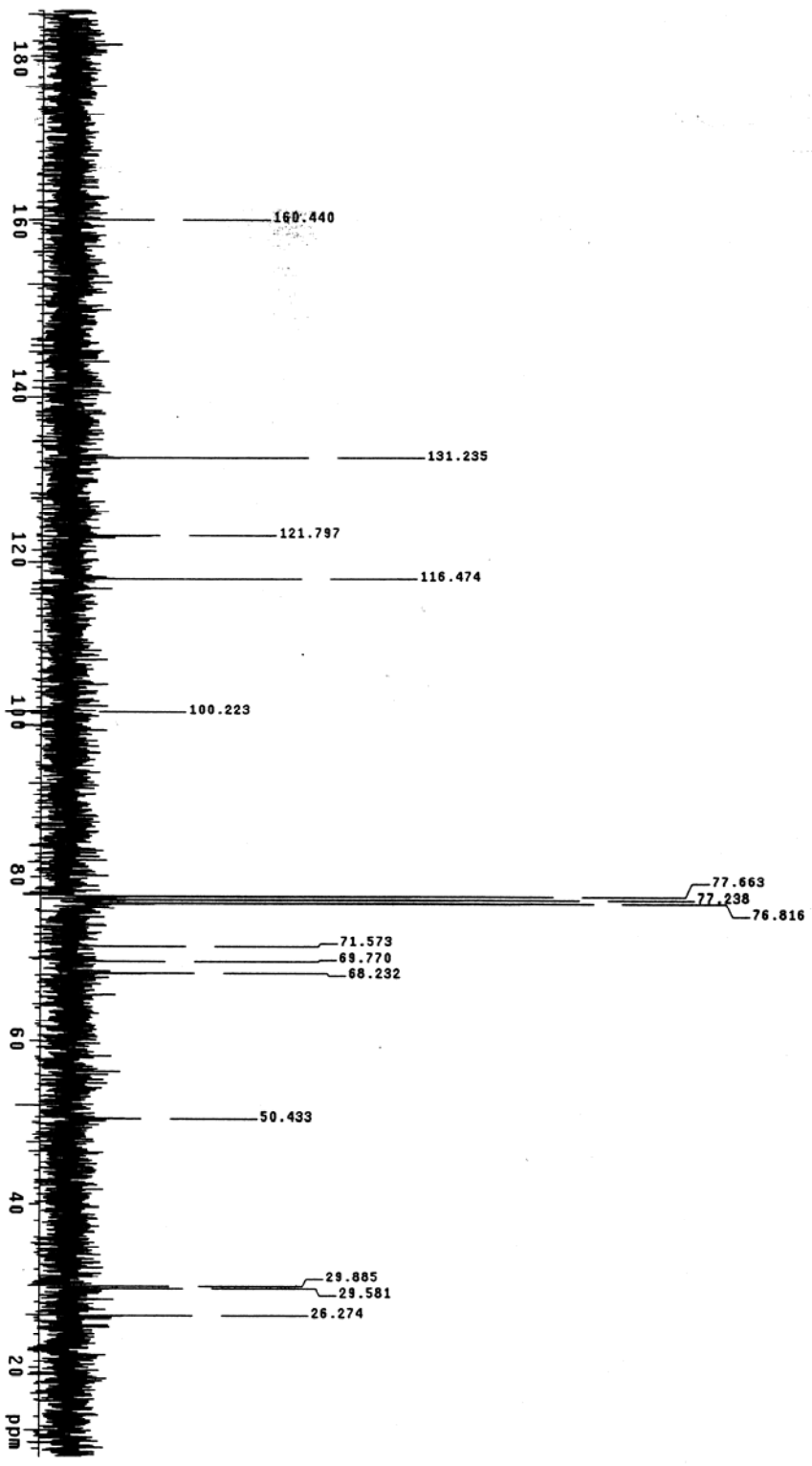
12-H·PF_6: Compound **11**-H·PF_6 (0.25g, 0.27 mmoles) was dissolved in a suspension of THF and PtO_2 (Adam's catalyst). The reaction was frozen, evacuated using vacuum, and warmed to room temperature. This process was repeated twice more. An atmosphere of hydrogen was placed over the reaction. The reaction was stirred a room temperature for 30 minutes. The reaction was filtered through a pad of celite and solvent removed under reduced pressure to yield **12**-H·PF_6as a light brown sticky solid (0.23 g, 90 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41 (d, J = 8.3 Hz, 4H), 7.06 (d, J = 8.3 Hz, 4H), 4.36 (m, 4H), 4.25 (m, 4H), 3.85 (s, 8H), 3.67 (t, J = 3.9 Hz, 4H), 3.62 (t, J = 6.9 Hz, 4H), 3.52 (m, 4H), 3.30 (t, J = 7.2 Hz, 4H), 3.23 (m, 4H), 2.91 (s, 4H), 2.11 (m, 4H), 1.73 (quintet, J = 6 Hz, 4H), 1.32 (m, 4H), 1.26 (s, 4H).

Acylated [2]catenane: Compound **11**-H·PF_6 (0.5 g, 0.54 mmoles), acetic anhydride (0.17 g, 1.6 mmoles) and triethyl amine (0.16 g, 1.6 mmoles) were dissolved in CH2Cl2 (0.01M). The reaction was stirred at room temperature for 12 hours. Solvent was removed under reduced pressure and the crude oil was purified by column chromatography (SiO_2: EA) to yield the acylated catenane as a clear oil (0.42 g, 95 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.316 (d, J = 8.4 Hz, 2H), 6.93 (m, 6H), 5.47 (m, 2H), 5.37 (m, 2H), 4.73 (s, 2H), 4.67 (s, 2H), 4.31 (t, J = 5.7 Hz, 2H), 4.20 (t, J = 4.5 Hz, 2H), 3.86 (m, 4H), 3.58-3.31 (m, 14H), 2.16 (s, 4H), 1.95 (m, 4H), 1.71 (m, 4H), 1.61 (m, 4H), 1.39 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.07, 158.27, 158.19, 130.12, 129.96, 129.74, 129.45, 128.36, 126.70, 115.268, 115.22, 114.52, 71.55, 71.41, 70.86, 70.77, 70.60, 70.52, 70.45, 70.34, 70.23, 70.20, 70.09, 69.72, 69.36, 69.20, 67.03, 66.70, 66.15, 53.74, 52.16, 30.42, 29.90, 29.63, 29.18, 28.85, 28.49, 26.49, 26.08, 24.60, 22.31. HRMS-FAB (m/z): [M + e] calcd for $C_{46}H_{74}NO_{11}$, 816.5262; found, 816.528.



12-H·PF_6

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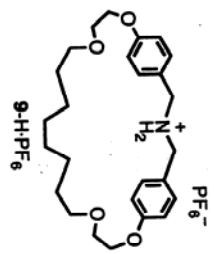
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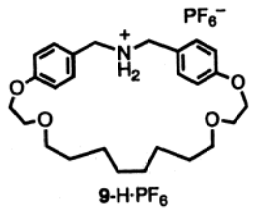

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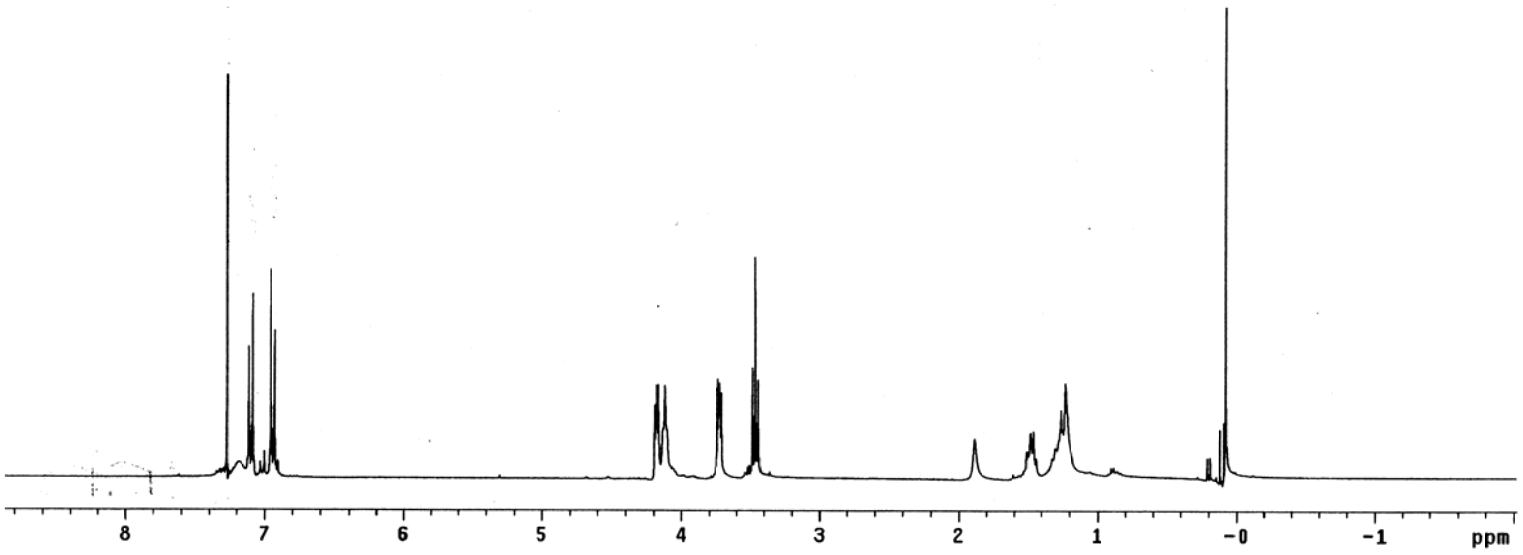

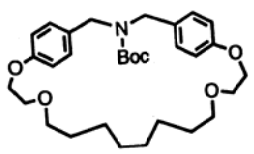
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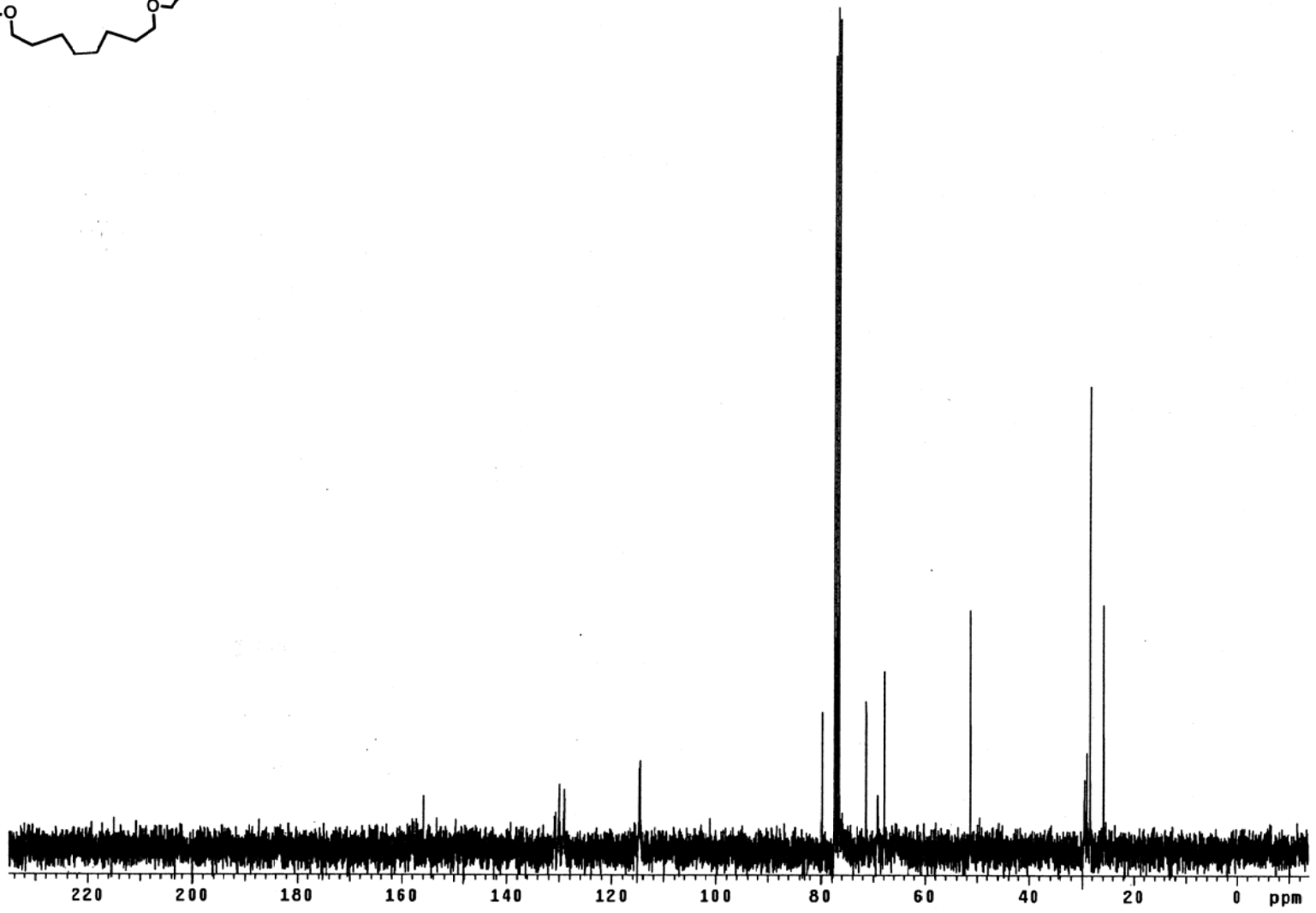
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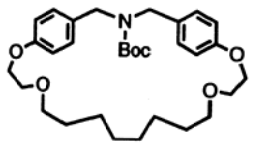
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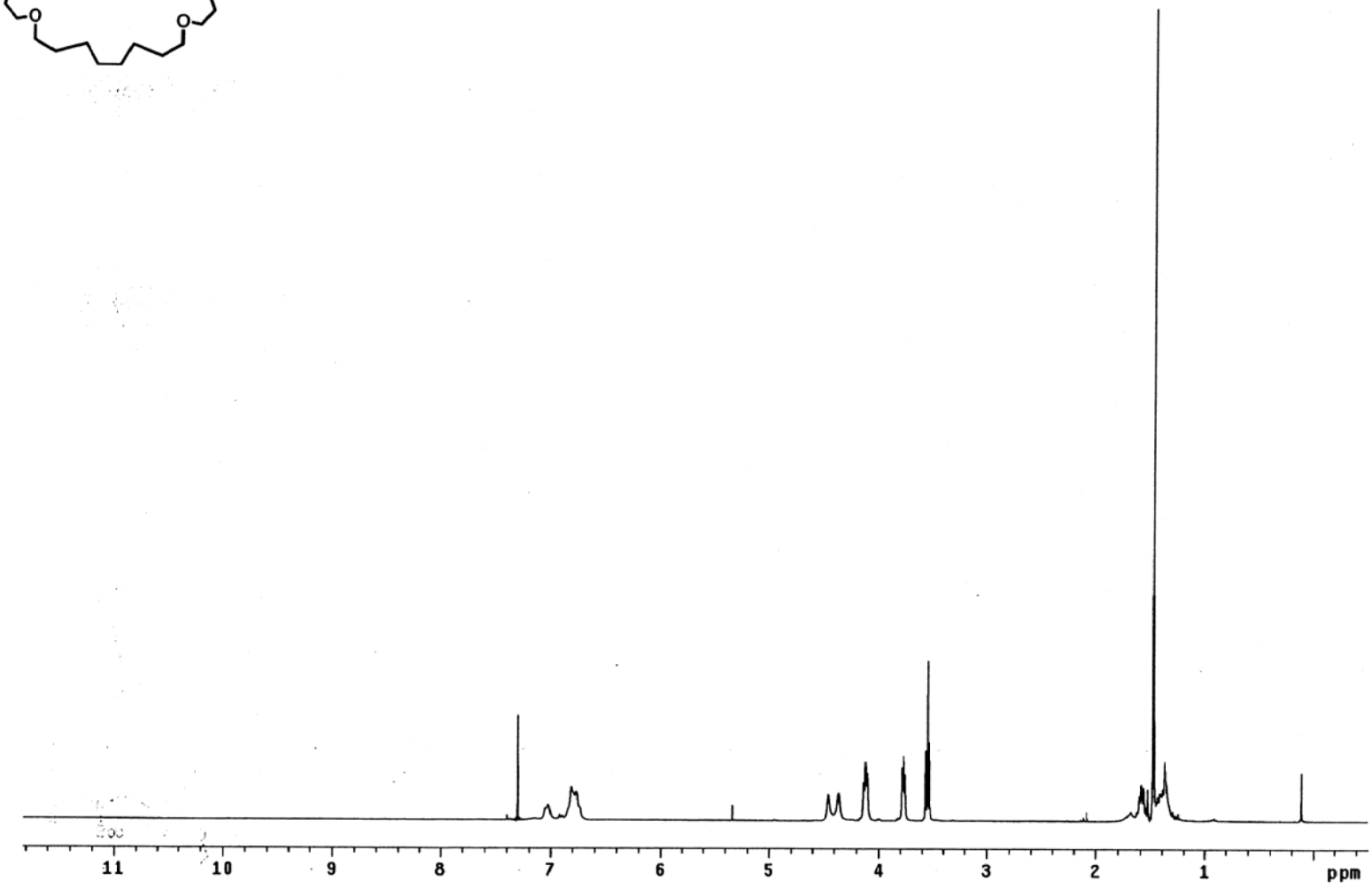
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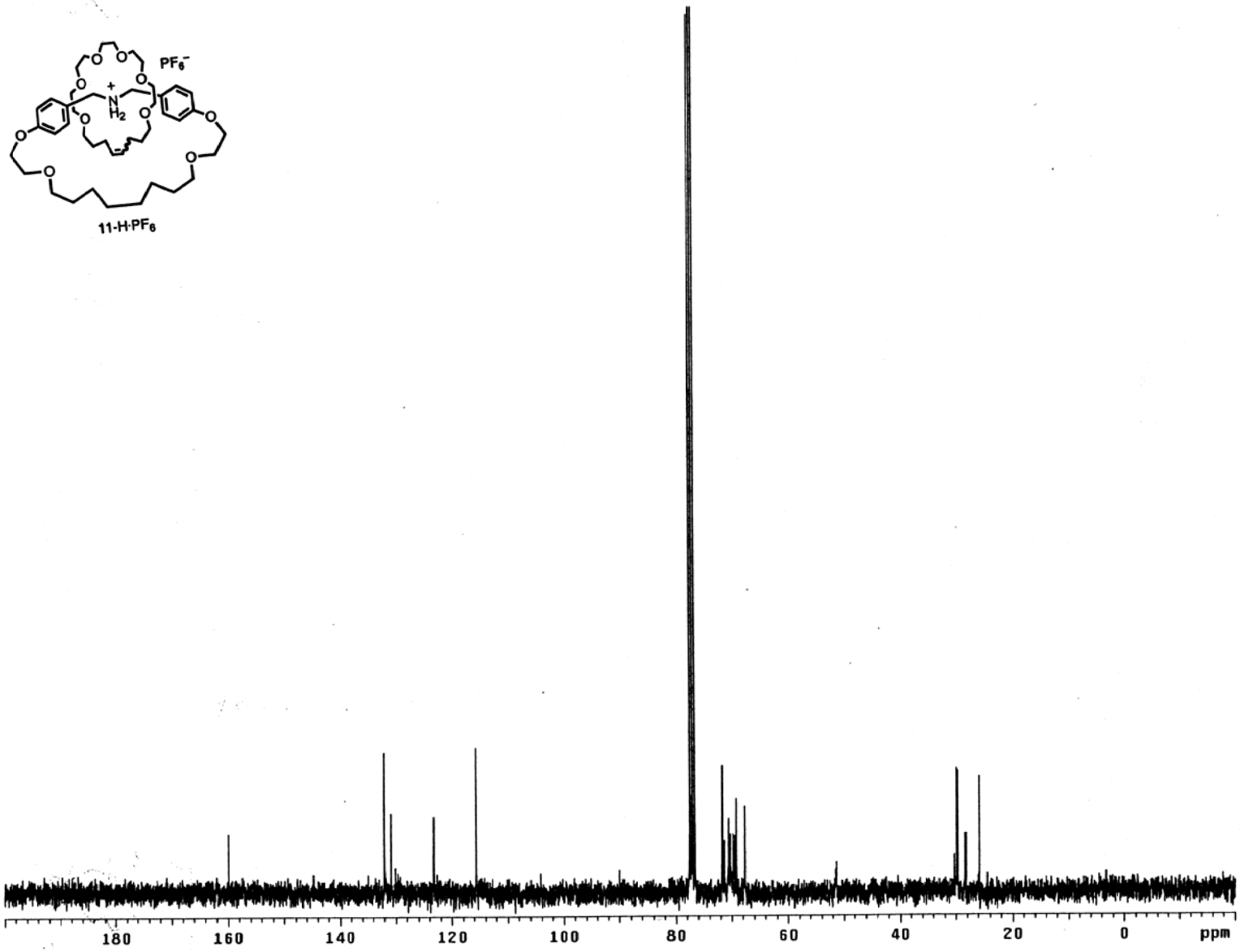
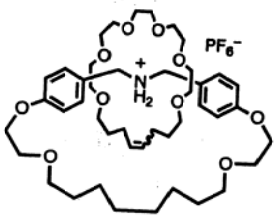
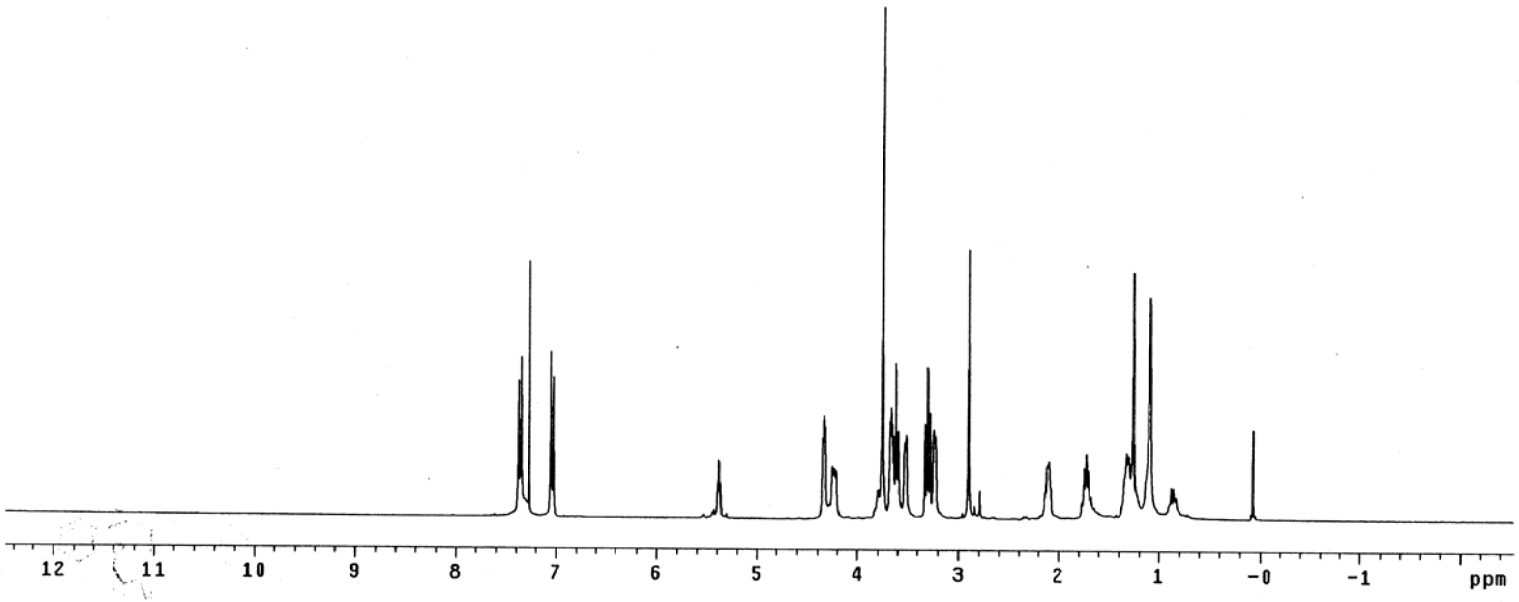
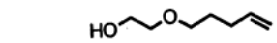
11-H·PF6





11-H·PF_6

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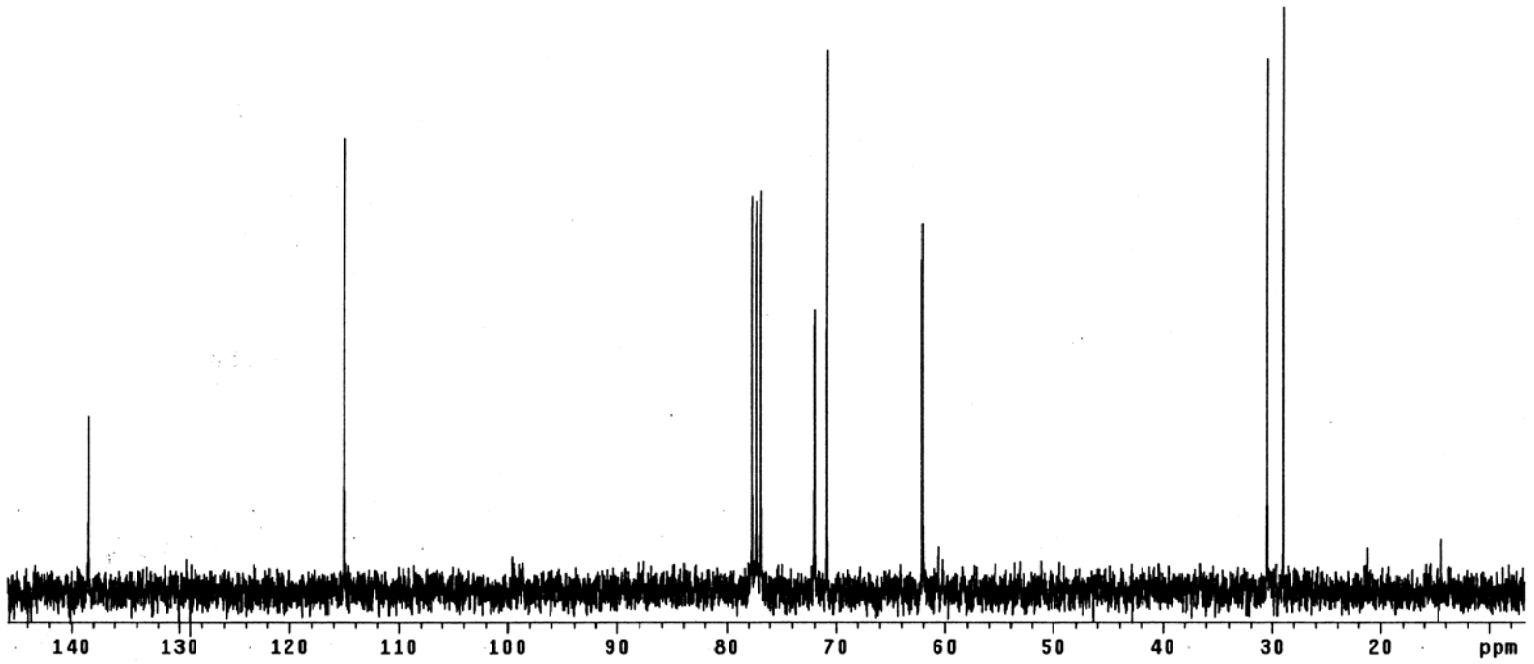
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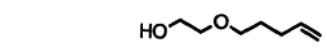
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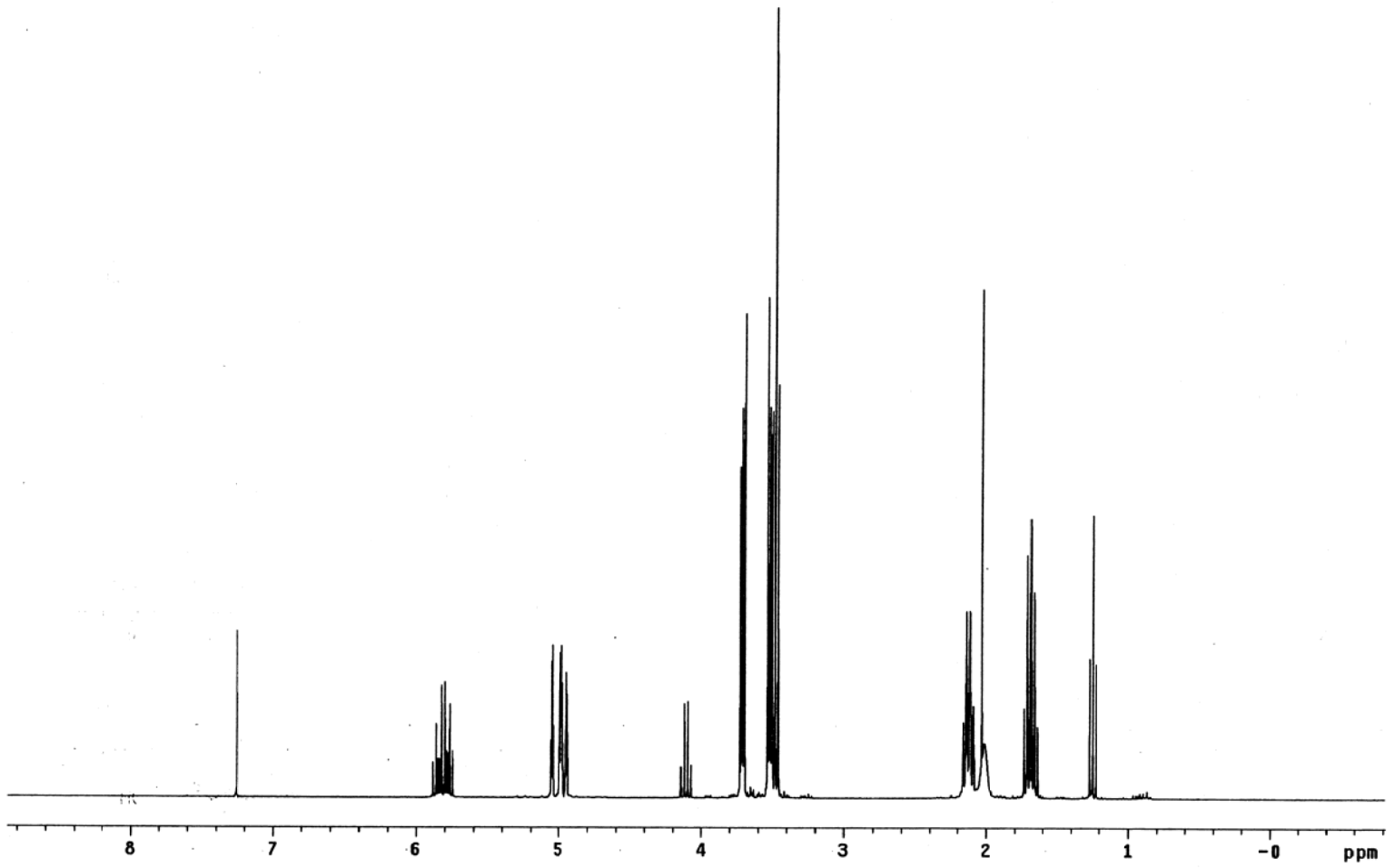
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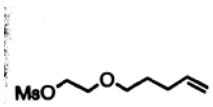

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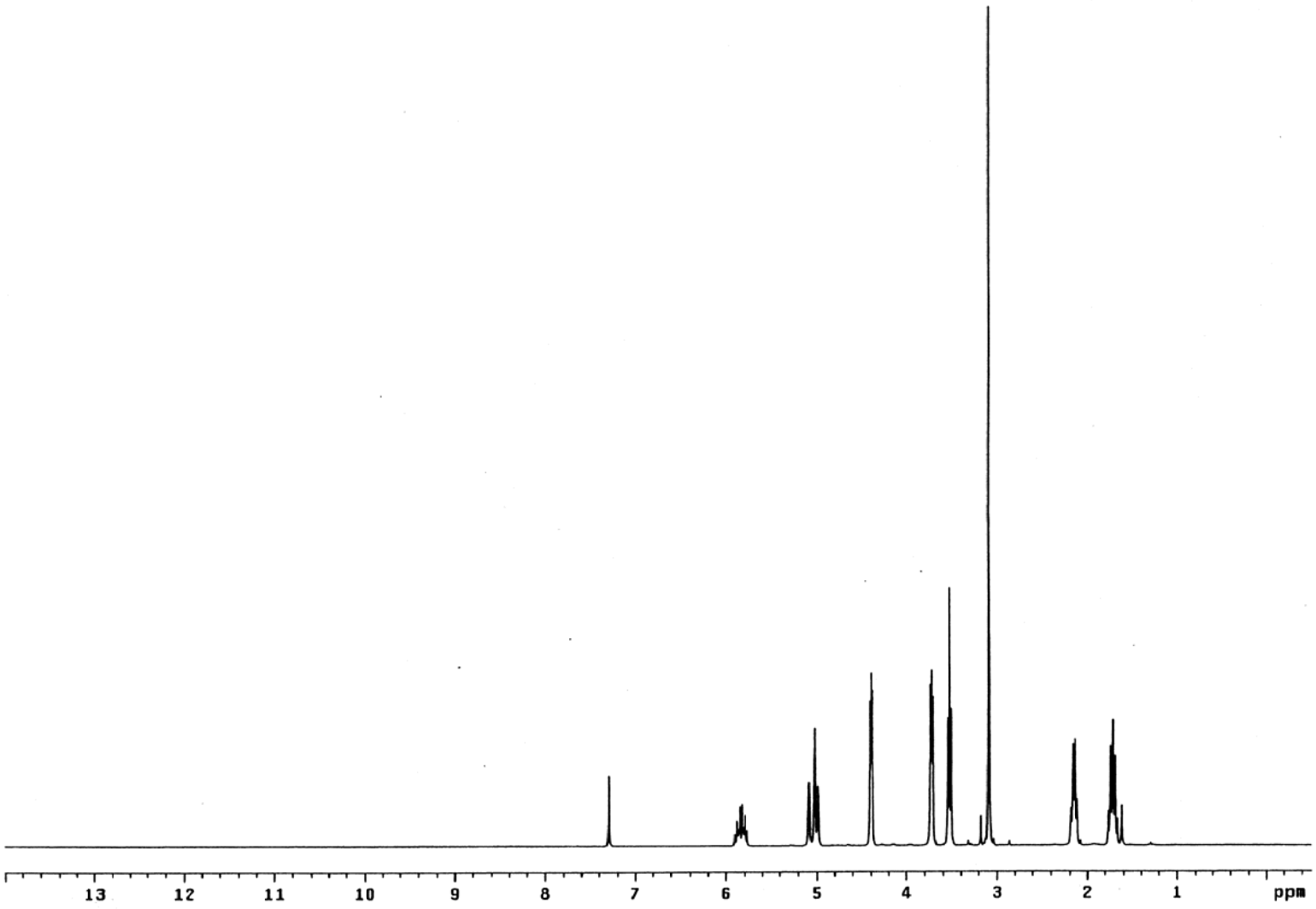

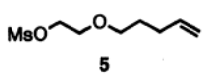

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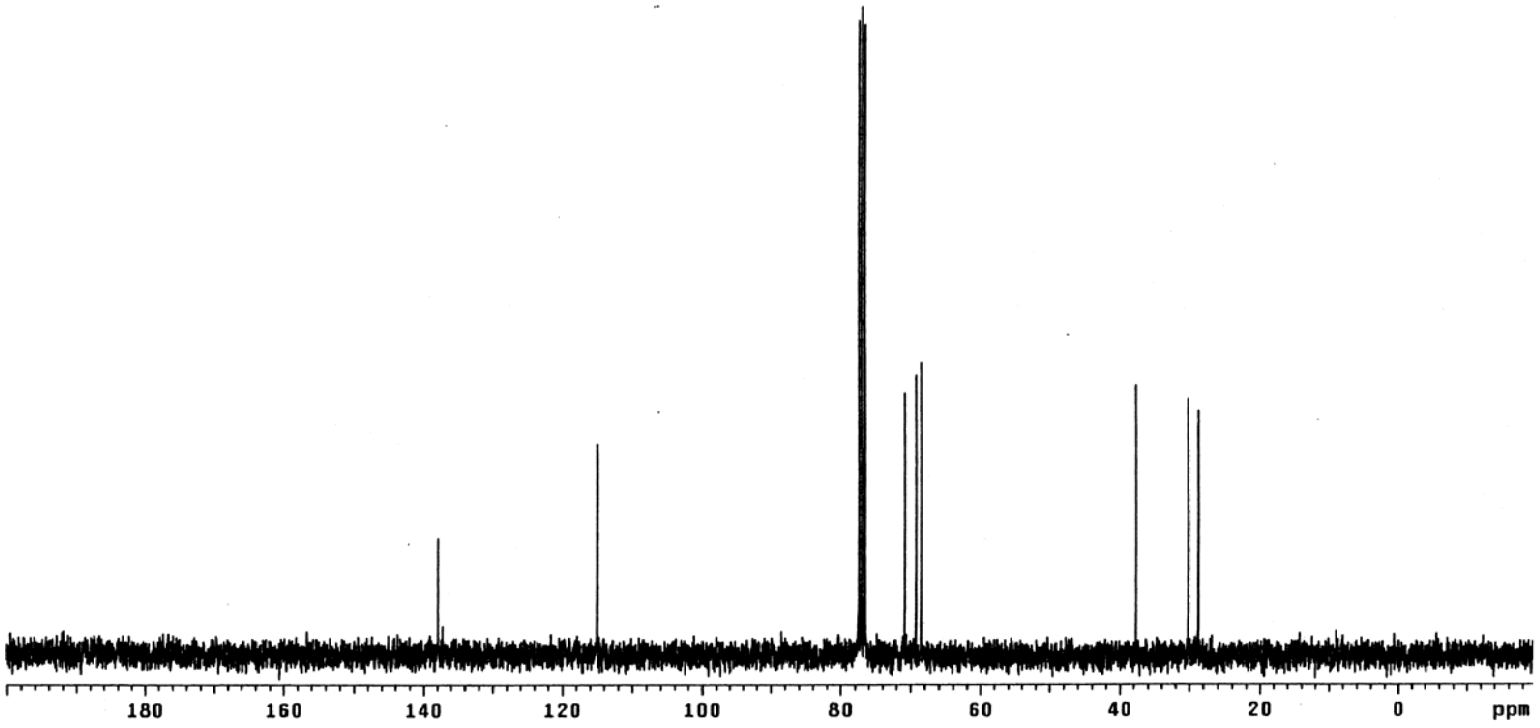

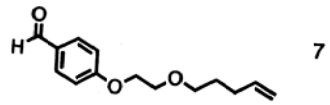

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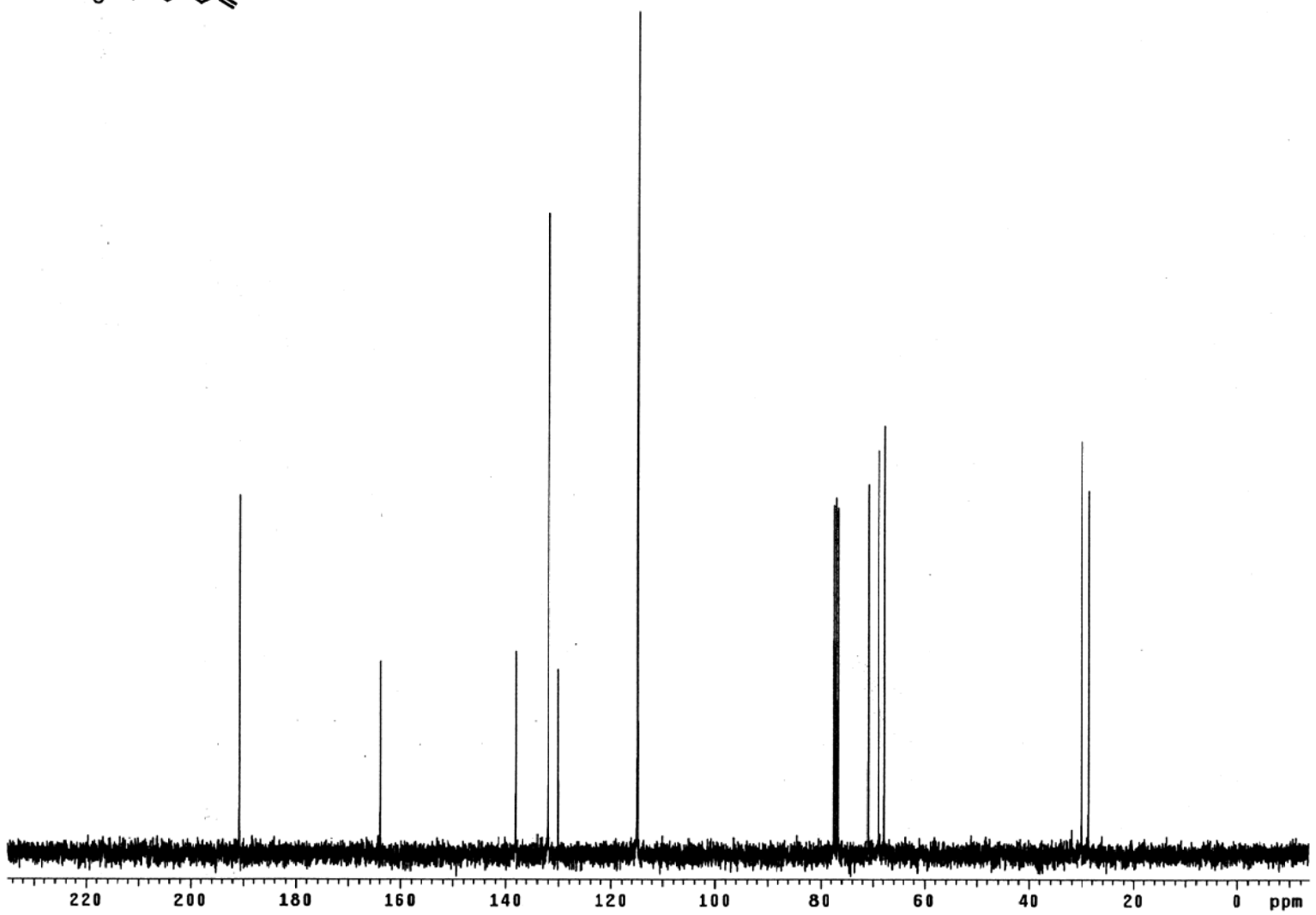

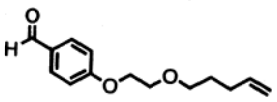

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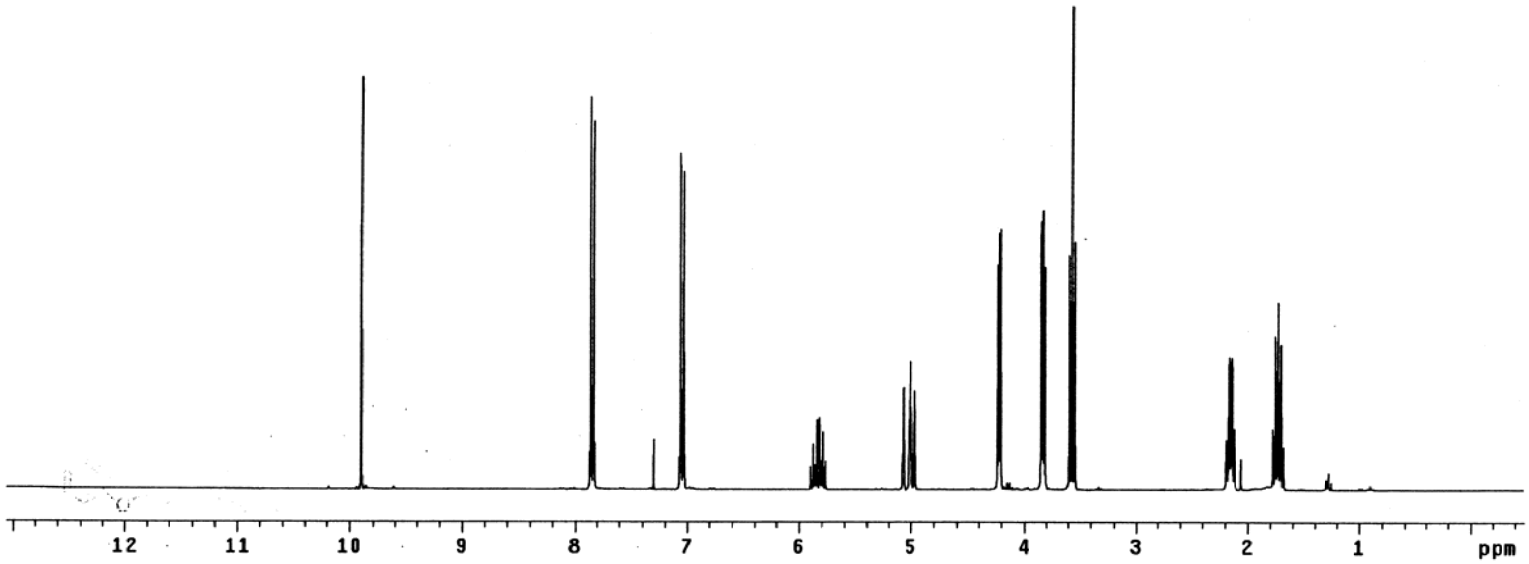

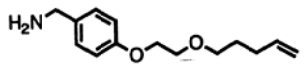

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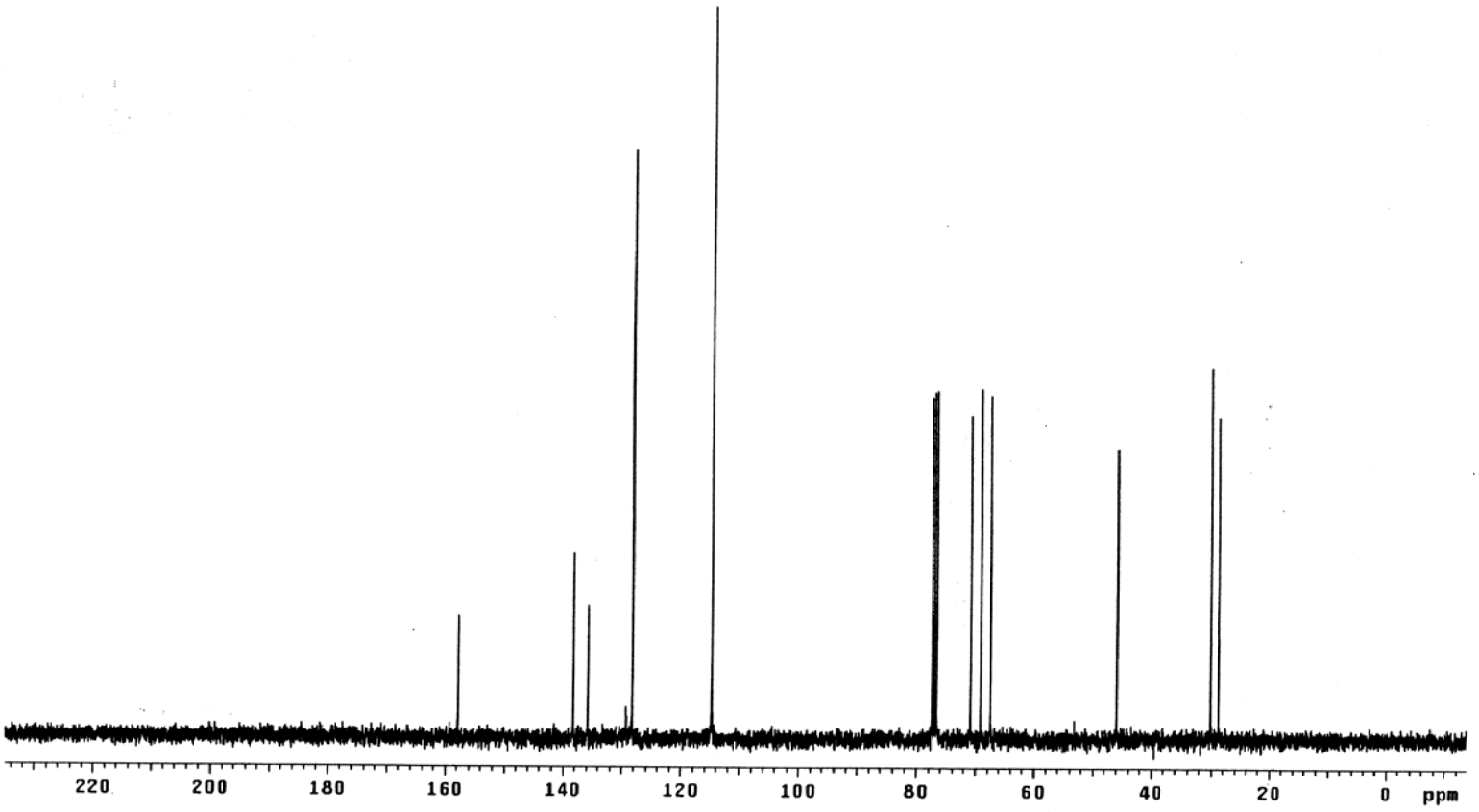

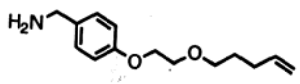
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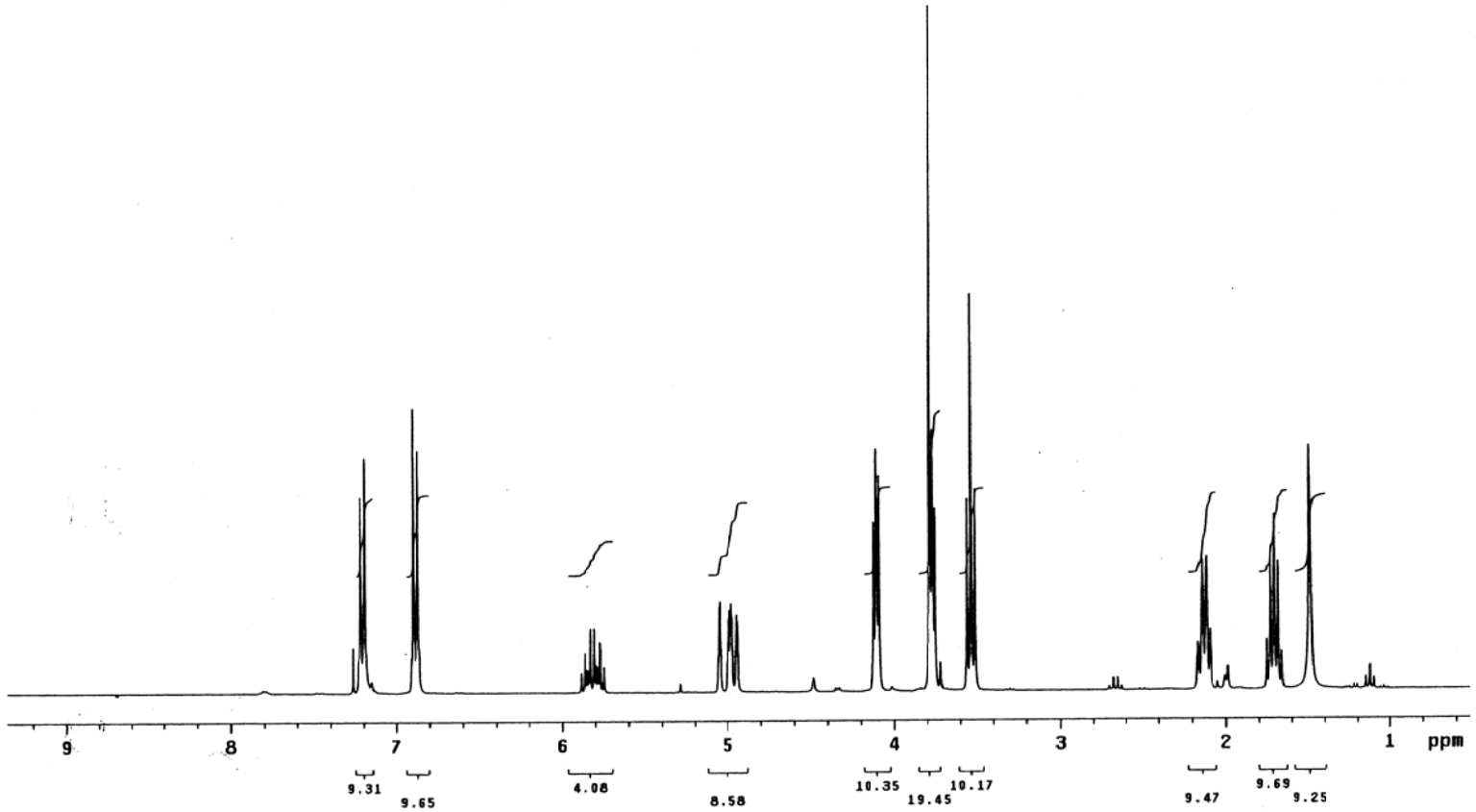
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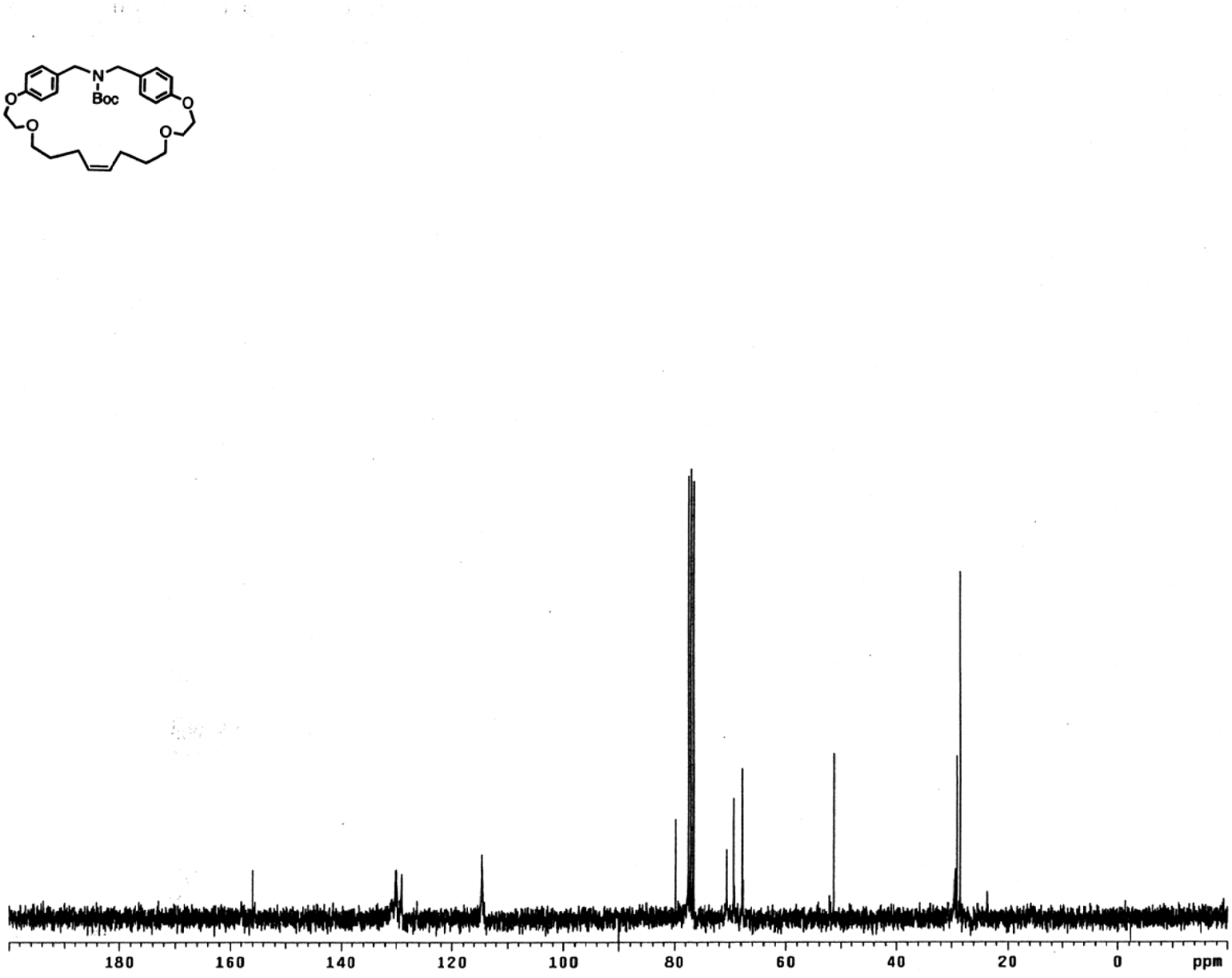
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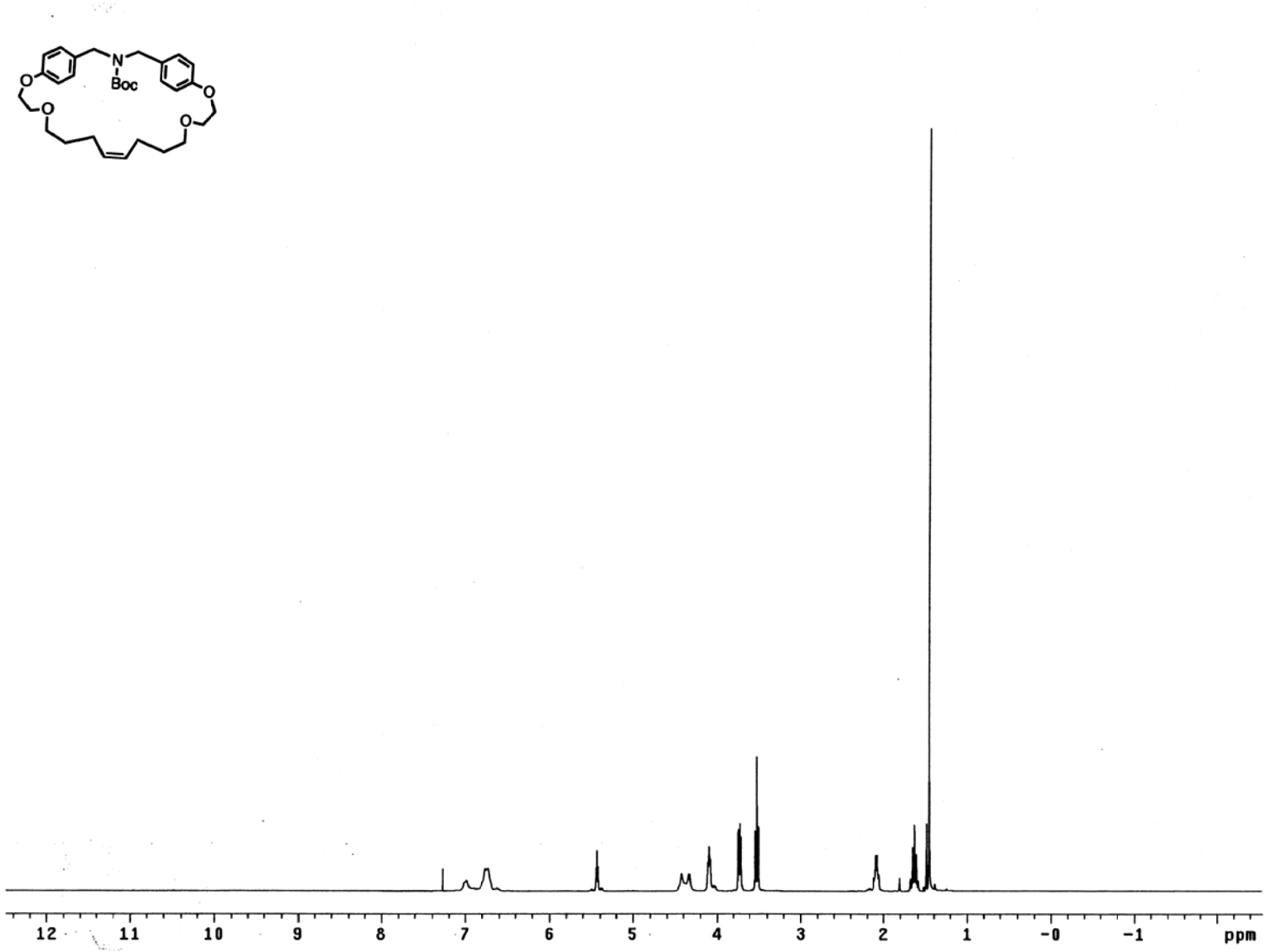
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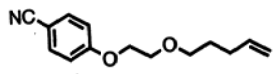
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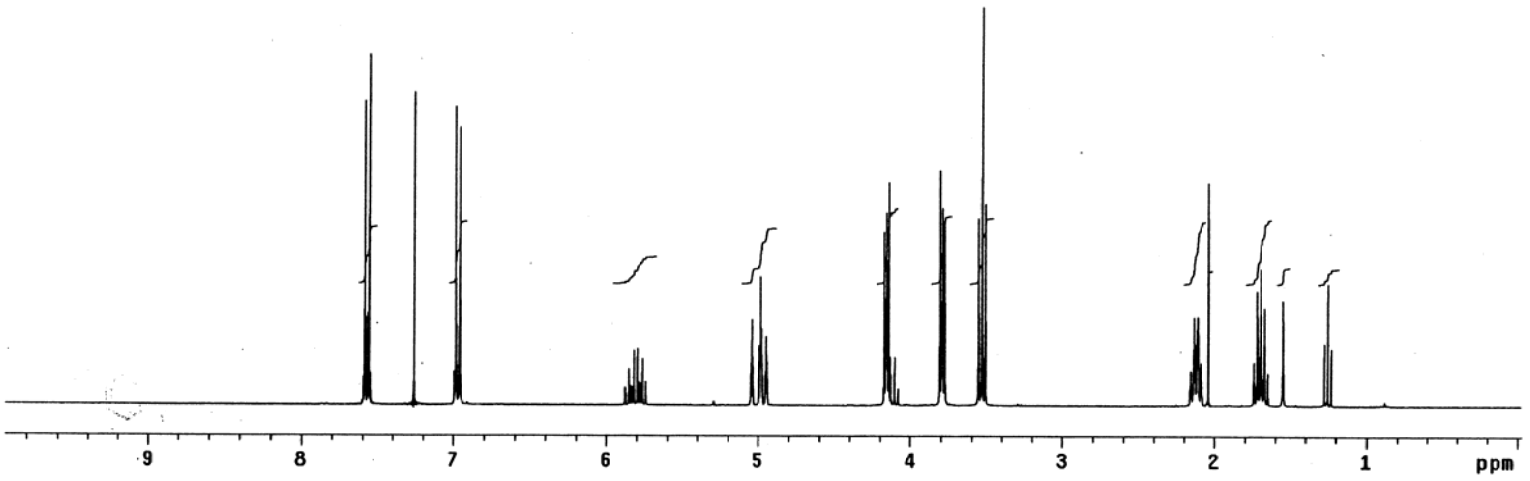
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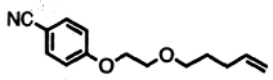
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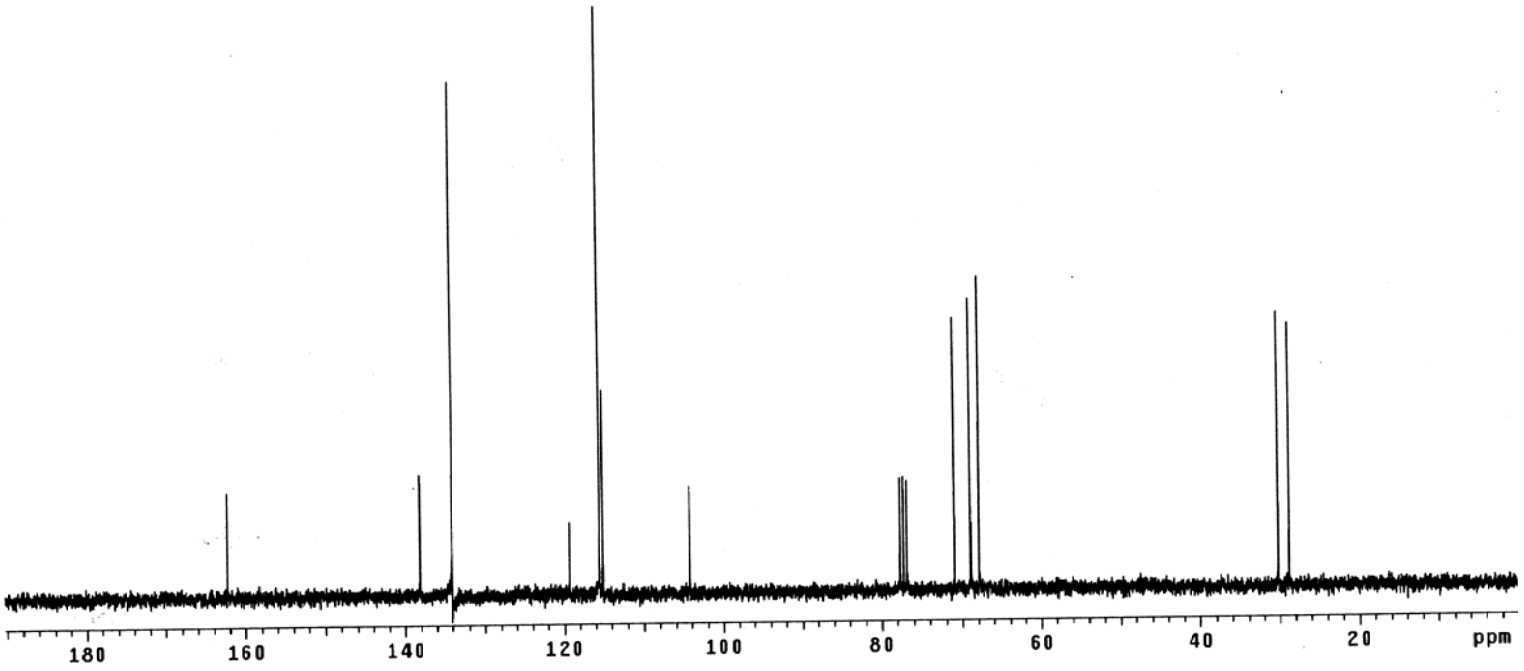
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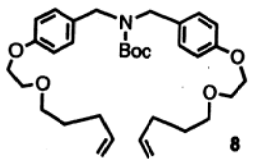

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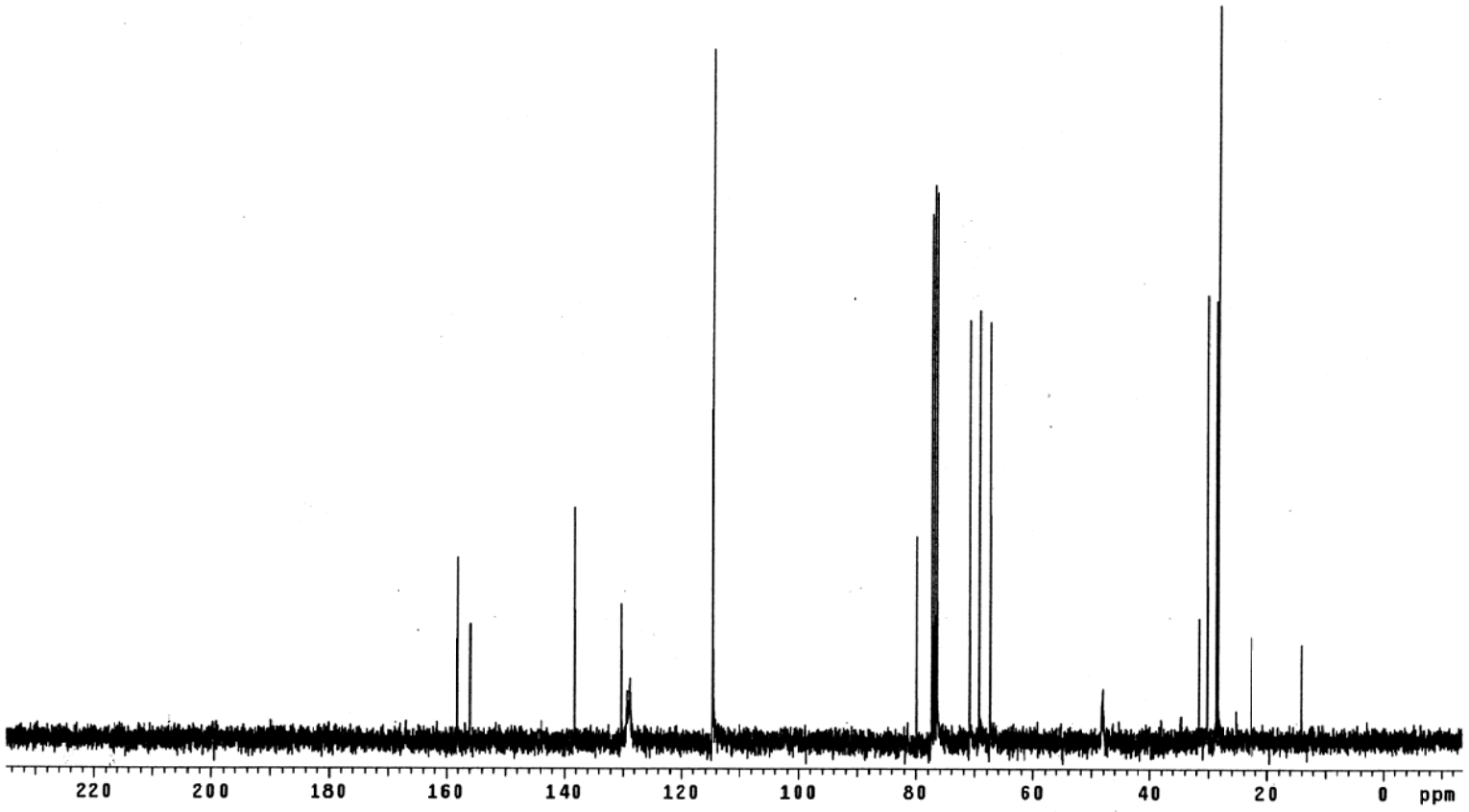

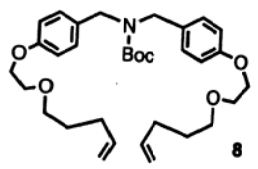

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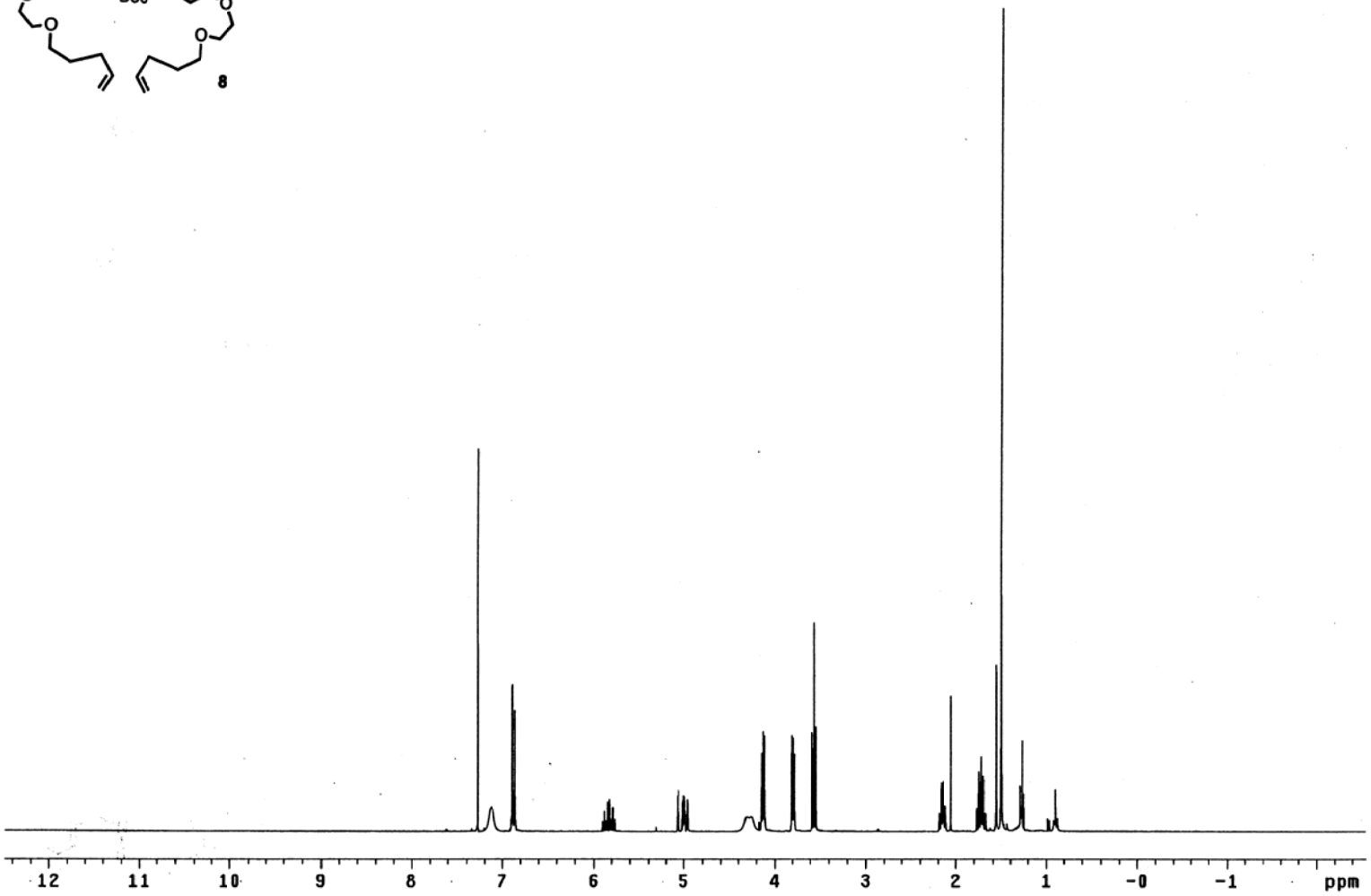

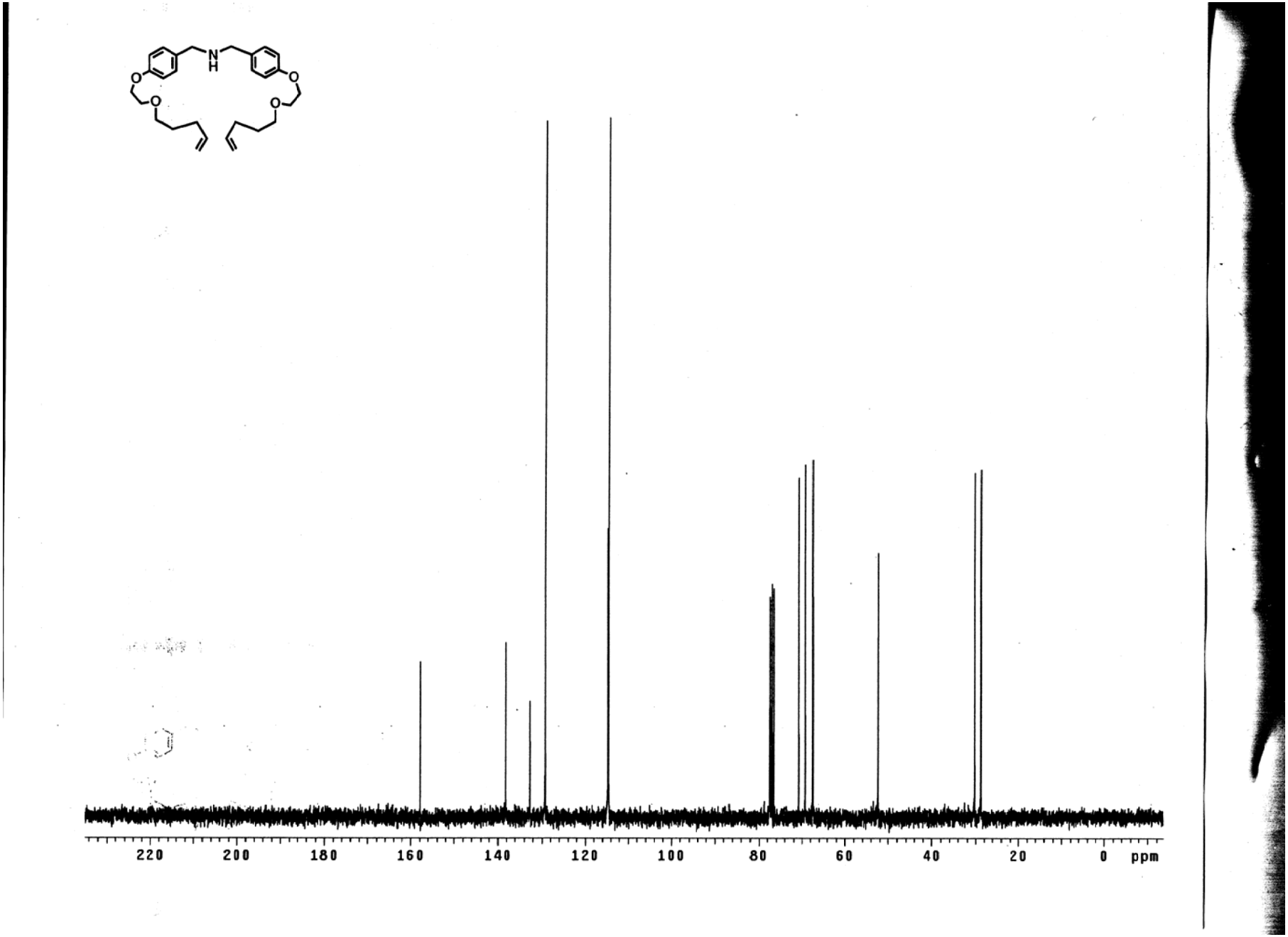
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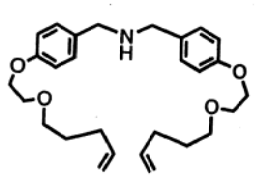
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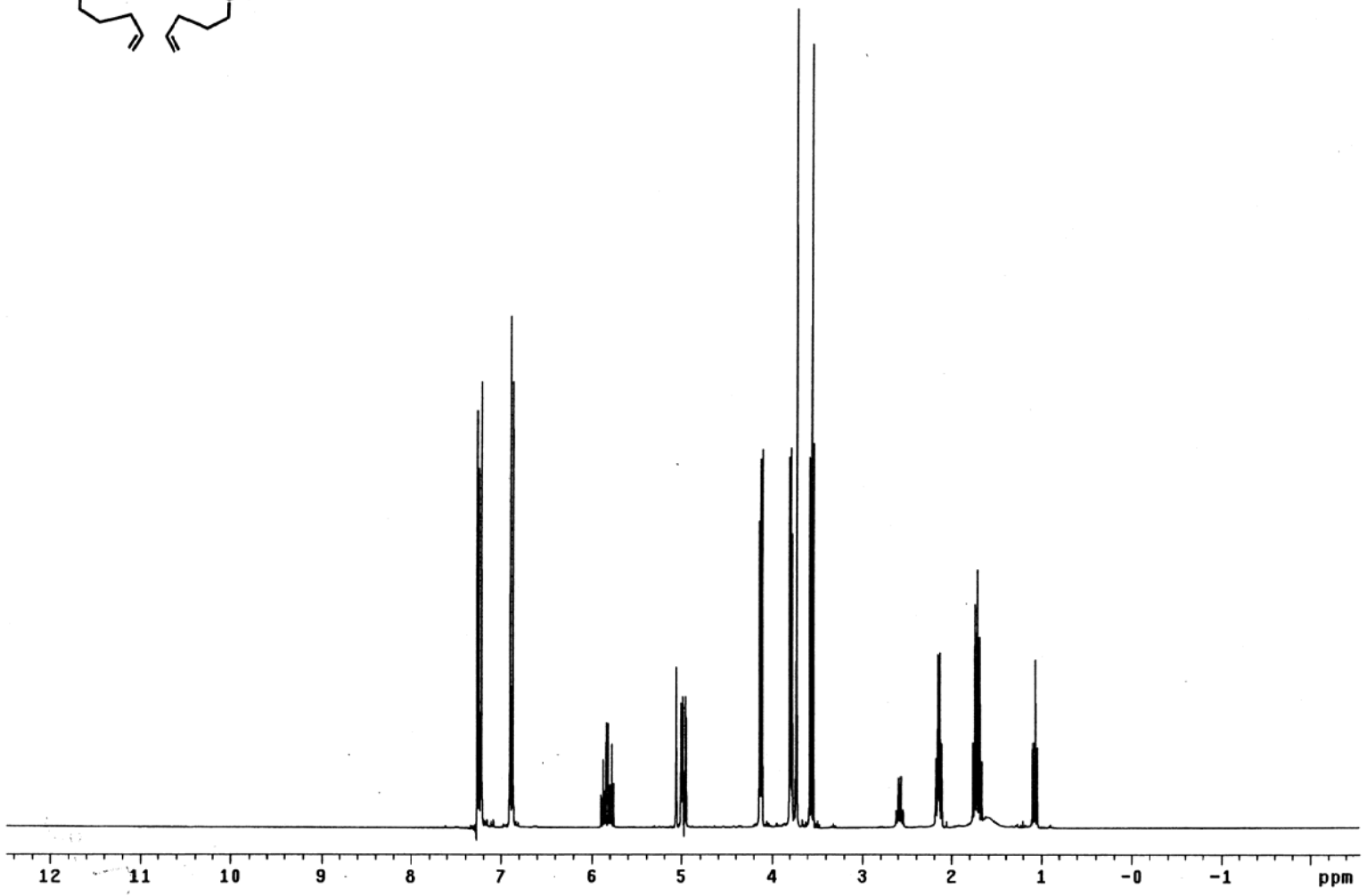
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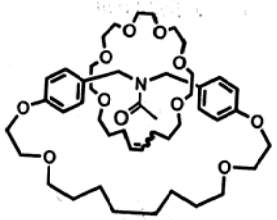
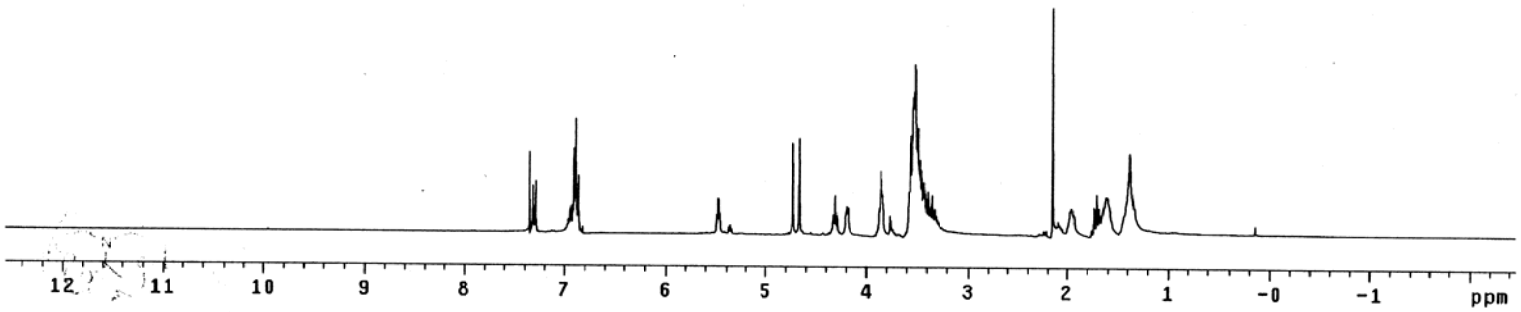
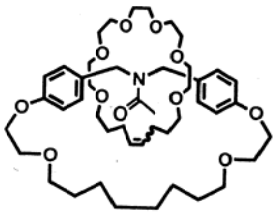


acylated [2]catenane





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